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EXPERIENCES IN HUNGARIAN CORUNDUM PRODUCTION

The following is a lecture delivered at the chemistry conference of 1951. It is followed by a series of four comments that appeared in the original.

Valter Harrach

The first experiments in corundum production in Hungary started in 1949 with a 4,400-kilowatt single-phase furnace. In 1950, making use of our knowledge gained at the experimental plant, we started production at the Mosonmagyarovar plant with a three-phase furnace. The purpose of this article is to discuss some of the problems which we came across during the tests and the production process. The short period which has elapsed in Hungarian corundum production shows how difficult it is to set up a plant that will produce according to the needs and desires of the buyer. The problems encountered may be classified as follows: raw material, production processes, and inspection methods.

Currently three types of corundum are produced: high-grade corundum, manufactured from fused alumina; regular-grade corundum with bauxite reduction; and black corundum, manufactured from bauxite without reduction.

In the manufacture of high-grade corundum, the fused alumina is crystallized while it is slowly cooled. It is of primary importance that the alumina should not contain any impure constituents and should not become impure during melting. For this reason we use graphite electrodes in the melting process.

We made a survey of the composition of the alumina used by certain plants, as well as an analysis of the corundum manufactured. The survey shows that there is only a slight change in the raw material during the melting process and that the change has an adverse effect on the quality of the corundum. At the Magyarovar plant, we had to use carbon electrodes for melting, since no graphite electrode of 600-millimeter diameter was available.

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The corundum obtained was grayish due to ash and carbon particles. After heating, the grains turned white; however, according to the users, they are more brittle than grains heated with graphite electrodes. The production of white corundum was unfavorably influenced by the formation of aluminates, especially $CaO.6 Al_2O_3$ and $Na_2O.12 Al_2O_3$, which diminish the corundum content and spoil its grinding quality.

Regular-grade corundum is produced by reduction melting. Under the influence of coal, the principal impurities in bauxite are reduced to metal and separate from the unreduced aluminum oxide. Domestic corundum produces can select from a wide variety of bauxite the most adequate kind. The various bauxites used in different carborundum-producing plants are listed in the following table (in percent):

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	Mois-ture	Loss by heat	$\frac{Al_2O_3}{SiO_2}$	Al_2O_3	SiO_2	Fe_2O_3	TiO_2	CaO	Bauxite Types
Carborundum Electrite, Benatky	--	11.73	30.2	57.05	1.89	25.51	2.98	0.90	Hungarian
Feldmuhle, Luisdorf	8.0	13.0	6.0	60.0	10.0	12.0	2.9	0.15	French
	15.0	14.0	9.1	58.5	6.4	'9.0	2.9	0.2	Hungarian
MSO, Rheinfelden	--	12.6	18.9	71.8	3.8	8.0	3.6	0.25	French
	--	-	10.9	60.12	5.52	17.01	2.35	0.35	Hungarian
Lonza Werke, Waldshut	13.55	15.1	6.7	58.21	8.71	14.70	2.87	0.11	Hungarian light
	14.75	14.67	9.8	57.14	5.82	20.78	2.87	0.22	Hungarian red
Ferrowerk Rhina, Lau-fenberg	--	12.0	11.1	57.5	5.2	22.0	2.7	0.07	French
	--	14.2	9.1	60.77	6.65	13.55	3.3	3.02	Hungarian
Elektroschmelzwerk /Electric Smelting Plant/, Zschornewitz	14.40	15.10	9.3	53.44	5.76	21.80	3.20	0.7	Hungarian
Corundum Factory, Dorog	--	14.5	7.4	61.48	8.36	11.82	2.70	0.29	Gant, roasted
	--	12.66	17.2	57.4	3.33	22.77	2.88	0.42	Devecser, roasted
	--	29.40	11.5	57.69	5.00	5.05	2.70	0.16	Devecser, raw
Corundum Factory, Magyarovar	--	13.15	16.8	57.58	3.42	22.61	2.69	0.41	Gant, roasted
	--	13.80	6.0	62.34	10.37	9.83	2.69	0.40	Gant, roasted

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In using various bauxites, especially with SiO_2 content, the impurities settled down inadequately and spread for the most part within the alumina ingot in small particles. First the bauxite was preroasted, but experiments with raw bauxite proved that roasting is not necessary and that in some respects it is even better to use raw bauxite. As a reducing substance, coke manufactured from domestic coal was used.

Foreign plants have an entirely different opinion concerning the reducing substance, but the entire industry agrees on the requirement that the ash content be kept to a minimum. The ash content of coke means the introduction of new impurities into the furnace, the elimination of which increases power consumption. Nevertheless several plants used coke with an ash content higher than 20 percent. The size of the coke we used first was 20-40 millimeters. We later used of a size of 10-20 millimeters, with an ash content of 16-20 percent.

In manufacturing colored corundum, auxiliary substances are necessary from time to time. For the formation of a magnetizable and well settling alloy -- if the SiO_2 content of the bauxite is very high (above 15 percent) -- the addition of iron chips brings the desired result. Bauxite used in Hungarian plants did not require the use of iron chips.

We also used sawdust in composing the mixture. The admixture of sawdust was especially advantageous with roasted bauxite, because it reduces the formation of deposits on the electrodes and loosens the structure of the deposit.

For the manufacture of both white and colored corundum, we used either graphite or carbon electrodes. While the quality of white corundum is greatly affected by the graphite electrodes, with colored corundum the improvement of the quality is not in proportion to the investment. We received carbon electrodes from Poland, Germany, and France. There is not much difference in their composition. Their ash content is between 3 and 5 percent; however, the French electrodes proved to be less resistant to exhaust gases than the German and Polish products.

In the manufacture of corundum, the electric power consumed plays and important part. It is advisable to apply very high tension to avoid power losses. While at 78 volts the furnace yielded only 78.7 percent of the theoretical productivity, when 130 volts were used productivity was 93 percent. According to the findings of Globukov, Konkakov, and Filomenko, the size of corundum crystals decreases rapidly with the increase of voltage. For this reason, the voltage limit of the furnace is 120-130 volts for normal electrocorundum In the furnaces of Dorog and Magyarovar, we achieved the best undisturbed melting with the application of 100 volts.

Reduction can be accomplished by two methods, namely, with the application of a constant amount of power while the quantities are decreased, or with an increasing amount of power while the quantities are maintained constant. The course of reduction is: first Fe_2O_3, then SiO_2, and TiO_2, and finally Al_2O_3. CaO mixed with Al_2O_3 forms CaO.6 Al_2O_3, and with SiO_2 and Al_2O_3 it forms anorthite $(CaO.Al_2O_3.SiO_2)$. The reduction of the CaO is as follows: $CaO + C = Ca + CO - 108,060$ calories.

In the course of reduction, calcium carbide, instead of calcium is obtained, because its formation is exothermic:

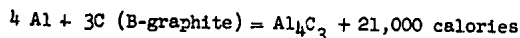$$Ca + 2 C \text{ (B-graphite)} = CaC_2 + 14,500 \text{ calories}$$
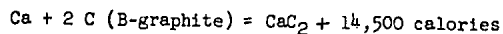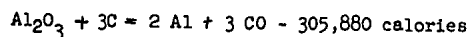
Because of the CaO content and the formation of anorthite and calcium hexaaluminate, CaC_2 is produced by excessive heating, i.e., overreduction, while at the same time Al_2O_3 is also being reduced partly to metallic aluminum and partly to aluminum carbide according to the following equation:

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$$Al_2O_3 + 3C = 2 Al + 3 CO - 305,880 \text{ calories}$$

$$4 Al + 3C \text{ (B-graphite)} = Al_4C_3 + 21,000 \text{ calories}$$

The Al_4C_3 and CaC_2 presumably become dissolved in the corundum bath and with the further processing of the granules they create impurities because of dissolution in water.

During our experiments, we melted some overreduced ingots and obtained ingots that pulverized under the influence of air in a few weeks. After these experiences, we returned to the normal process and gave up the idea of lowering the Fe_2O_3 content of corundum below 0.5 percent by purely metallurgical methods. Reduction of Al_2O_3 cannot be avoided entirely, because the ferroalloy always contains metallic aluminum. In melting, the production of the alumina is 91 percent, which may be explained by the fact that in the zones of the electric arcs alumina-producing conditions prevail.

As a result of reduction, the corundum contains 94-98 percent Al_2O_3 and and a variable combination of Fe-Si-Ti-Al alloy. To obtain corundum granules which will satisfy the grinding industry, we have to confine the composition of the ingots to certain limits. The Hungarian plants which use corundum have the following requirements for corundum granules:

Composition	White Corundum		Colored Corundum
		Maximum Percent	
Al_2O_3	$99 \pm \frac{1}{2}$		96 ± 1
Fe_2O_3	0.15		1
CaO	0.25		0.2
SiO_2	0.25		2
MgO	0.5	$(TiO_2) \longrightarrow$	3 ± 1

It is simple to obtain this composition for white corundum by melting the Magyarovar alumina with graphite electrodes. By using carbon electrodes, unfortunately, too many impurities get into the corundum, and for this reason we cannot always meet the requirements of the Fe_2O_3 content.

In case of regular-grade corundum, the requirements in regard to Al_2O_3, SiO_2 and CaO can be met through purely metallurgical methods. This cannot be done in regard to Fe_2O_3 and TiO_2. If we perform the reduction in such a way that the Fe_2O_3 content falls below one percent, then we cannot avoid the reduction of part of the TiO_2, and the desired TiO_2 content of 3 percent will not be reached. On the other hand, if we wish to obtain the TiO_2 content, the Fe_2O_3 content will increase above the prescribed limit. Foreign plants have solved the problem by leaving the TiO_2 unchanged during reduction. They oxidize FeO left in the block by heating it to magnetizible Fe_2O_3 and then removing it by a repeated magnetizing process.

In our plant, the final treatment of the granules had not been introduced as yet, and it has been possible to separate iron from the granules by magnetization only. The final heating has another advantage, namely Al_2C_3 is oxidized to Al_2O_3, and the cracks can be avoided in the ceramic disks.

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Some plants treat the disk with an acid solution, whereby not only its iron content but also its TiO_2 content decreases. This treatment is more expensive than final calcination. We have experimented with the acid method with the following result:

We used technical concentrated hydrochloric acid. The use of concentrated HCl is not economical in a big plant. We can get better results if we do the acidification in two phases, first with diluted and then with fresh, more concentrated acid.

	Original Corundum	Treated With Used Acid (percent).	Treated With Fresh Acid
Al_2O_3	86.4	91.9	93.98
SiO_2	2.76	2.74	2.16
Fe_2O_3	6.83	1.70	0.85
TiO_2	3.65	3.30	2.85

The final treatment has the further advantage that reduction does not have to be carried too far and the granules stay firm. Synthetic corundum granules are cemented together by a glassy substance and the higher the alumina content, the more rigid the substance. The table below compares the composition of corundum manufactured in foreign plants with Hungarian granules. We must stress the fact again that all plants apply final treatment.

	Al_2O_3	SiO_2	Fe_2O_3	TiO_2	CaO
			(percent)		
Corundum Electrite, Benatky	95.288	1.37	0.65	1.45	1.14
Feldmuhle, Luisdorf	96.2	0.8	0.6	2.4	--
Ferrowerk Rhina, Laufenberg	96.28	1.04	0.07	2.65	--
Electroschmelzwerk, Zschornewitz	96.04	0.48	0.77	1.35	0.85
			Ingots		
Snythetic Corundum	97.50	0.31	0.73	1.20	0.22
			Granules		
Magyarovar	96.15	0.68	0.94	1.85	0.22

Magyarovar corundum granules usually contain more impurities than the average ingot. The reason is that the magnetic selection is not perfect and iron-alloy granules remain among the corundum granules.

The manufacturing plants also require that the granules should not stick together when heated to 1,300 degrees centigrade. Other requirements concerning the granules will be given when dealing with the inspection methods. First, however, let us discuss ferroalloys as a by-product of corundum production.

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The alloy which forms during the melting process subsides in part to the bottom of the bath and forms particles containing a greater or smaller amount of silicon, aluminum, titanium, sulfur, and phosphorus. All these substances are present in the melting raw material. The amount of alloy depends on the quality of the bauxite. During melting, more alloy will be formed if the deposit contains a great deal of impurities, especially SiO_2. While from bauxite with a 3 percent SiO_2 content we obtain 90-100 kilograms of alloy for each ton of corundum, the quantity increases to 500 or 550 kilograms in the case of bauxite with a SiO_2 content of 10 percent. The corundum industry has the following requirements in regard to the alloy: (1) the complete elimination of impurities should be speeded up and the reduction process made easier, and (2) the alloy should be easily separated from the corundum during melting and also during further processing.

The iron alloy in Hungarian corundum production used to contain 5-18 percent silicon, 1.5-9 percent aluminum, 1.5-14 percent titanium, and small amounts of sulfur and carbon. These wide variations existed because, as mentioned before, we had some overheated, extremely reduced blocks, in which the TiO_2 and Al_2O_3 were also greatly reduced. Now, having more experience in this respect, the Al content of the alloy does not exceed 4 percent and its Ti content is also lower.

The high Al and Si content of the alloy, besides being a warning against excessive reduction, has another danger. namely, the two metals greatly reduce the magnetizing and settling properties of the alloy. An alloy of 15-20 percent Si content cannot ordinarily be magnetized and the same applies to an alloy with a 4.5 percent Al content. Separation of iron from the corundum granules is therefore difficult.

We tried to find connections between the specific gravity and magnetizability of the iron alloy. Unfortunately we did not find well-defined limits, because the relation of the components in the alloys changes. An alloy below a specific gravity of 6 did not show magnetizing properties, while among alloys with a specific gravity between 6 and 6.5 we found some that were magnetizable and some that were not.

We offered the iron-alloy ingots for testing purposes to iron foundries, but they did not accept the ingots because of the varying composition. In Germany they are used for the production of acid-resistant castings, because an alloy with a Si content of over 10 percent resists the effects of sulfuric or hydrochloric acid.

It is evident that many factors influence reduction, even under normal conditions. Clearly, the plants need well-trained technical experts and workers. According to the report of a foreign plant, a corundum melt ruined a furnace only twice in 26 years. In Hungarian plants, on the other hand, we have had several bad experiences during 2 years of operations.

Tests made during production do not give much help to the technical management. Labortory findings can generally be known only after the processing period. Only the analysis of the raw materials must be given to the plant manager before melting starts. Substances to be analyzed are bauxite, coke, alumina, and electrodes. In examining the raw materials, moisture, and water of hydration, as well as the Al_2O_3, Fe_2O_3, SiO_2, TiO_2, CaO, and S content, are important. During melting, the expert metallurgist tests the progress of reduction. Unfortunately, we do not have sufficient experience in this respect. Analysis of the iron alloy and corundum block is made after melting. The SiO_2, Fe_2O_3, and V_2O_5 content of the corundum is analyzed by using a mixture of K_2CO_3 and Na_2CO_3. The Al_2O_3 content is also analyzed.

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The Si, Ti, and Al content in the iron alloy is determined and the magnetic test is made. Further processing is done in the light of the information obtained concerning the Si, Ti, and Al content. If the alloy is not magnetizable, none of the corundum with iron content is allowed to be ground. In case of magnetizable alloy, separation of the iron could be left to the magnetizing separator and the carborundum with iron content can be ground too. After cutting, grinding, and classification of the ingots, we obtain the finished granules, which are the basic material of the grinding industry.

After classification, the granules are packed in sacks. Final examination of these granules is the responsibility of the consumer. In our plant we take a sample from each kind of granule every day and laboratory tests determine the components, just as with the blocks. In addition, we take weekly samples of all granule types. Besides the chemical tests, we determine the granulometric composition of the granules, according to Soviet standards. If the grading is adequate, no more than 15 percent of the granules may be one size larger than norm, no more than 20 percent may be one size smaller, and no more than 15 percent three sizes smaller.

The structure and shape of the granule are examined by microscope. We ordered a polaroid microscope, which will enable us to examine the mineralogical composition of the granule.

Fire-resistance tests of the granules are also prescribed. The granules must not stick together or crack at 1,300 degree centigrade and must meet the requirements of sifting analysis, even after heating.

Iron content is determined by the baking of cakes. We mix the granules with a ceramic binder and water, form a cake, and heat it at 1,300 degrees centigrade for an hour. The baked cakes should not contain any iron particles. The iron particles appear in the disk in the form of spec..s and may cause corrosion during the grinding process. Requirements concerning the strength of the granule are not yet specified.

Once we know the results of the chemical analysis, an acid test required by the grinding-disk factories is not important, because the iron content determined by dissolution in hydrochloric acid and precipitation by NH_4OH would not give exact results concerning the iron content determined in the course of extraction.

Hardness is determined by the pendulum sclerometer, which has a diamond bearing. It is placed on the substance to be tested and hardness is determined by the decrease in the amplitude of oscillation.

The most reliable test for determining the quality of the granules is grinding with a testing disk. In this test, a disk is made from granules of a given size and hardness and is compared with a disk made from standard granules in a grinding test.

Two very simple but clever testing methods of the Soviet Scientific Research Institute for Grinding Materials may be mentioned, which have not been applied in Hungary as yet, but which we intend to apply in the future:

1. To determine the grinding capacity, granules of a given weight are rubbed on a glass disk. The grinding capacity can be figured out from the loss of weight of the disk.

2. To determine the rigidity, the grinding material is rubbed between two steel plates for a certain length of time. The rigidity is calculated on the basis of the quantity of granules which fall apart.

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COMMENTS

1. By Dr Tihamer Gedeon

After World War II, Hungary had great difficulties in obtaining abrasives. It was then decided to produce corundum in Hungary.

In 1947, the State Aluminum Board dealt with the problem and in November of the same year preliminary plans were submitted to the National Planning Office. Because of the urgency of the problem, a credit of several million forints was granted and a committee was created to work out the details. In the spring of 1949, the Directorate of the Fine Ceramics Industry called a meeting, at which the lack of corundum was discussed. Enthusiastic experts formed a brigade for the establishment of granule production and this group converted a small 400-kilowatt carbide furnace in the Dorog Carbide Plant for synthetic corundum production. Experiments were started in July 1949, and after one month of experimenting, the Dorog plant became a regular producer. This small plant produced only clear white corundum at the beginning. In mid-December it began experiments with the production of colored corundum, using the iron-deficient bauxite of Gant.

The lecturer discussed the chemical problems of synthetic corundum production, but we can follow the struggles involved in the production better if we know something of the equipment needed. The furnace differs greatly from other electric furnaces; its main characteristic is that corundum is not drained from the furnace. The furance is very simple, consisting of an iron cart rolling on tracks and carrying a 30-80 centimeter thick carbon-brick bottom, on which a water-cooled conical iron shell is placed. The iron shell is unlined and as far as we know only one plant, in Benatky, Czechoslovakia, is operating with lined shells. The operation starts in the furnace with the formation of an arc from the two or three electrodes and this arc is covered with alumina or a bauxite-carbon mixture. After sufficient heating, the melting starts. The furnace is generally operated by three-phase current.

In the corundum production method described above, the melted corundum is cooled for 16-24 hours. The shell is removed and, after another 24 hours, the pig is removed by a crane and taken to be crushed.

When preparing the mixture for the manufacture of colored corundum, we have to figure out the amount of carbon needed for the reduction of the iron oxide and silicon dioxide content. The quantity of carbon has to be calculated carefully, because the carbon content of the electrode also takes part in the reduction. Too much carbon could cause carbide formation and later lead to the pulverization of the corundum ingot. During melting of the corundum, part of the silicon dioxide becomes silicon monoxide and evaporates from the furnace. Coming into contact with air, the silicon monoxide again becomes silicon dioxide and settles on the electrodes and in other parts of the plant as a white powder. Unfortunately, the collection of this colloid-like silicon dioxide is neglected during the process. It is a very active substance, readily soluble in caustic soda solution and suitable for the production of silica gel.

The lecturer did not speak about the power requirements for synthetic corundum. The requirement is 1.5-2.0 kilowatt-hours per kilogram for melting white corundum from alumina heated at 1,200 degrees centigrade. Colored corundum made from bauxite requires more power, because the substance must be kept in a molten stage until the iron reduction is completed. The energy requirement for colored corundum is 3.5-4.2 kilowatt hours per kilogram. The consumption of electrodes is about the same in both types of corundum, namely 3.5-4.5 percent for white and 3.5-5 percent for colored corundum.

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Colored synthetic corundum may be produced by the use of Söderberg type of electrode. It is well known that the Söderberg electrode is less expensive and requirements for electrodes in corundum production are not so high as in aluminum metallurgy. Such electrodes can be produced from domestic raw materials.

2. By Alfred Romwalter

In supplementing Dr Gedeon's comments, 1 want to mention that there must be a lot of calcium carbide besides SiO_2 in the smoke.

The selection of coke used in the reduction process is governed by the ash content. Preference is given to coke in which the ash contains the most SiO_2 and the least CaO and MgO, for the reason that SiO_2 can be eliminated by reduction, but CaO and MgO cannot. The presence of the latter two substances spoils the quality of the granules.

For the elimination of the iron oxide from domestic corundum, I suggest the addition of Fe-Si-Ti-Al alloys. By this method, we have a chance for eliminating the iron oxide in large amounts without causing any carbide formation.

3. By Laszlo Mattyasovszky-Zsolnay

The corundum industry is indebted to Harrach not only for the attempt to solve technical problems but also for working scientifically on a problem on which reliable technical literature is practically nonexistent. The grinding quality of the granules depends on their hardness and toughness. The main problem is how to obtain a granule of 96-percent hardness. The best foreign granules partially pulverize after 40 hours' grinding, while the Magyarovar granules pulverize partially after 4 hours' grinding. To find the answer to this problem we need more experience in both theory and practice.

Previous speakers discussed the importance of CaO and MgO and also the role of large crystals. However, a hard and very rigid corundum does not contain too much CaO or MgO. The difference is in the TiO_2 content. It is possible that by increasing the titanium content we can get the required toughness of a 96-percent-hard granule. I suggest that the capacity of titanium bauxite to increase toughness be scientifically determined and that the TiO content be increased.

4. By Ervin Becker

I would like to call the attention of my colleague Harrach to the Czernovitz Corundum Plant, which used a very simple but successful method. The essence of this method is that the test is made with an iron stick 20 millimeters in diameter, fastened to a wooden pole; the stick is dipped into the melt and tested while cooling. From the color of the melt and its density, the stage of the reduction can be determined. I observed that the good test separated easily from the iron stick and had a glassy, pale-yellow surface. According to reports from this plant, the method is very reliable in determining the stage of reduction.

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